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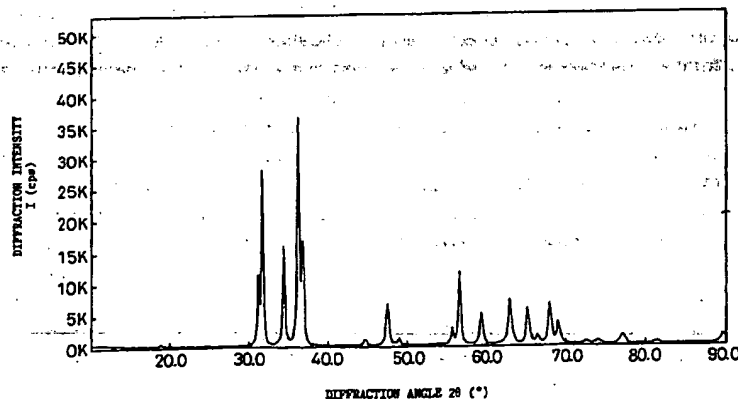
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Shiga 524-0021 (JP)**(54) ELASTIC POLYURETHANE FIBER AND PROCESS FOR PRODUCING THE SAME**

(57) An elastic polyurethane fiber comprising, based on the fiber weight, from 0.5 to 10% by weight of composite oxide particles containing aluminium and at least one combination of zinc and magnesium selected from the group consisting of combinations of zinc and magnesium in respective specific ratios. The elastic polyurethane fiber has excellent chlorine resistance, and is suitable for swimwear for use in swimming pools.

The elastic fiber can be obtained by spinning a polyurethane spinning dope containing, based on the polyurethane, from 0.5 to 10% by weight of the composite oxide particles. Filter clogging and yarn breakage caused by secondary agglomeration of the composite oxide particles are extremely decreased, and stabilized spinning can be conducted over a long period of time.

Fig.1

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improvement.

[0010] An object of the present invention is to provide an elastic polyurethane fiber having excellent chlorine resistance over a long period of time after dyeing under an acidic dyeing condition (pH 3 to 6) or after dye-fixation treatment with a tannin solution (pH 3 to 4.5) subsequently to dyeing, and a process for stably producing the same.

## Disclosure of the Invention

[0011] As a result of intensively carrying out investigations to solve these problems, the present inventors have found that an elastic polyurethane fiber comprising, based on the polyurethane, 0.5 to 10% by weight of composite oxide particles which comprise bivalent metal  $M^{2+}$  wherein  $M^{2+}$  is at least one metal selected from the group consisting of zinc and magnesium, and aluminium, and in which the molecular ratio of the bivalent metal  $M^{2+}$  to aluminium is from 1 to 5 not only has still more excellent chlorine resistance than the elastic polyurethane fiber to which the additives mentioned above are added, but also shows, astonishingly, that filter clogging and yarn breakage during spinning caused by secondary agglomeration of the composite oxide particles in the spinning dope are extremely reduced. They have therefore found that the elastic polyurethane fiber can be stably produced.

[0012] The composite oxide particles of the present invention can be produced by known methods. For example, the following methods are included therein: a method comprising melting a mixture containing zinc oxide, magnesium carbonate, aluminium hydroxide, etc. at 1,600°C, annealing the molten mixture at 600°C, and cooling the annealed material slowly (Journal of Non-Crystalline Solids, 129, 174-182 (1991)); a method comprising firing a mixture containing zinc oxide and  $\gamma$ -aluminium hydroxide at 900 to 1,000°C (Journal of Japan Ceramic Society, 91 (6), 281-289 (1983)); a method comprising adding lithium chloride, ethyl silicate and hydrochloric acid to an aqueous solution of magnesium nitrate and aluminium oxide to effect reactions, and firing the reaction products at 700 to 1,300°C (Chemistry Express, 5 (11), 885 to 888 (1990)); a method comprising spraying a solution of magnesium nitrate and aluminium nitrate in ethanol into a tube heated at temperatures from 740 to 1,030°C to effect reactions (Ceramics International, 8, 17-21 (1982)). Composite oxides having various compositions and morphologies can be produced by suitably setting starting materials, a composition ratio of the starting materials, a reaction (firing) time, reaction (firing) temperatures, etc. Particularly preferred production examples are methods for firing specific composite compounds as disclosed in Japanese Examined Patent Publications (Kokoku) Nos. 51-37640 and 51-20997.

## Brief Description of the Drawings

[0013] Fig. 1 is a powder X-ray diffraction pattern diagram of  $3ZnO \cdot ZnAl_2O_4$  (fired at 900°C). Fig. 2 is a powder X-ray diffraction pattern diagram of zinc oxide. Fig. 3 is an electron microscopic photograph of  $3ZnO \cdot ZnAl_2O_4$  (fired at 900°C). Fig. 4 is an elementary analysis chart of the crystalline grain A in Fig. 3.

## Best Mode for Carrying Out the Invention

[0014] The composite compound of the present invention is a precursor of a composite oxide, and signifies a compound which is capable of being oxidized in the course of firing the composite compound to form the composite oxide. Typical examples of the composite compound are hydrotalcite compounds known as composite hydroxides.

[0015] The present invention will be explained below by taking as examples composite oxide particles obtained by firing hydrotalcite compounds as composite compounds. However, the present invention is not restricted to the examples.

[0016] One example of a hydrotalcite compound used in the present invention is represented by the formula (1):

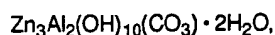


wherein  $M^{2+}$  is Zn or Mg,  $A^n$  is an n-valent anion such as  $OH^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Fe(CN)_6^{3-}$ ,  $CH_3COO^-$ , an oxalate ion and a salicylate ion, n is the valency of the anion,  $x > 0$ ,  $0 < z \leq 2$ , and  $m > 0$ .

[0017] The composite oxide particles in the present invention are obtained by firing the hydrotalcite mentioned above. Zinc is preferred because zinc has chlorine resistance higher than that of magnesium and imparts thereto a low degree of swelling for chlorine water. The composite oxide of the present invention can be produced by the production methods disclosed in Japanese Examined Patent Publication (Kokoku) Nos. 51-37640 and 51-20997.

[0018] The composite oxides obtained by firing hydrotalcite compounds in which  $M^{2+}$  is zinc will be explained as appropriate examples.

[0019] Preferred examples of the hydrotalcites containing zinc and aluminium include:



theoretical value (57.1%).

[0030] The solid solution represented by the formula (2) forms a structure in which aluminium oxide is dissolved in zinc oxide, namely, a structure in which aluminium is partially substituted into the sites of Zn in the zinc oxide crystals.

[0031] The elastic polyurethane fiber containing composite oxide particles in the present invention shows extremely decreased elution of the additives under acidic (pH 3 to 6) dyeing conditions or under dye-fixation treatment conditions with a tannin solution (pH 3 to 4.5) as compared with an elastic polyurethane fiber containing zinc oxide or solid solution of magnesium oxide and zinc oxide; moreover, discoloration of the elastic polyurethane fiber and the swelling amount thereof in chlorine water are extremely slight. Furthermore, the elastic polyurethane fiber in the present invention exhibits an excellent effect on chlorine resistance over a long period of time even when it is exposed to a chlorine bleaching agent, germicidal chlorine in a swimming pool, or the like.

[0032] The composite oxide of the present invention exhibits such excellent effects for the reasons explained below. When the composite compound is a hydrotalcite compound, firing the hydrotalcite compound forms a solid solution of zinc oxide and aluminium oxide (hereinafter referred to as (Zn, Al)O solid solution) or makes  $\text{ZnAl}_2\text{O}_4$  fine eutectic crystalline precipitate as eutectoid on the surface of zinc oxide. These substances are thought to play a protective role in the strongly acidic dyeing treatment or treatment with a tannin solution. Aluminium partially substituted for zinc and  $\text{ZnAl}_2\text{O}_4$  as eutectoid suppress a high agglomeration energy of zinc oxide, and exhibit an excellent effect of preventing secondary agglomeration; as a result, the composite oxide is thought to suppress filter clogging and yarn breakage, and the elastic polyurethane fiber can be produced stably.

[0033] Fig. 3 is an example of the electron microscopic photographs of the composite oxide  $3\text{ZnO} \cdot \text{ZnAl}_2\text{O}_4$  obtained by firing  $\text{Zn}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 3\text{H}_2\text{O}$  at  $900^\circ\text{C}$ . It is evident from the photograph that  $\text{ZnAl}_2\text{O}_4$  crystals are of eutectoid on the surface of hexagonal plate-like crystals of zinc oxide. Fig. 4 is a chart showing the elemental analysis of the crystalline grain A in the photograph of Fig. 3, and zinc and aluminium are detected. Figs. 3 and 4 are a photograph and a chart, respectively, obtained by observing and conducting analysis using an electron microscope (trade name of S-4100, manufactured by Hitachi Ltd.) equipped with an X-ray microanalyzer (trade name of EMAX-2770, manufactured by Horiba Ltd.) (acceleration voltage of 25 kV, magnification of 6,000, carbon deposition).

[0034] The present invention is characterized by that the composite oxide particles mentioned above are contained in an amount of 0.5 to 10% by weight based on the elastic polyurethane fiber. The composite oxide particles show an insufficient effect of chlorine resistance when the content is less than 0.5% by weight, and they not only exert adverse effects on the physical properties of the fiber but also increase yarn breakage during spinning when the content exceeds 10% by weight. A more preferred content is from 2 to 8% by weight.

[0035] The composite oxide in the present invention is more effective for the chlorine resistance when it has a smaller particle size, and the production stability is increased because filter clogging and yarn breakage during spinning become extremely rare. The average particle size is preferably  $5\text{ }\mu\text{m}$  or less. When the average particle size exceeds  $5\text{ }\mu\text{m}$ , filter clogging and yarn breakage tend to take place. It is more preferred to make the average particle size  $1\text{ }\mu\text{m}$  or less by wet grinding the composite oxide in a polar solvent such as dimethylformamide or dimethylacetamide.

[0036] For swimwear made up of knitting of an elastic polyurethane yarn and a polyamide fiber, in order to prevent discoloration and fading caused by chlorine after dyeing, the swimwear is usually treated with a tannin solution to fix the dye on the fiber after dyeing. The tannin solution acts to dissolve and remove metal oxide used as an anti-chlorine agent of the elastic polyurethane fiber from the fiber. In order to prevent such action, the surface of the composite oxide particles of the present invention are preferably treated with such substances disclosed in Japanese Unexamined Patent Publication (Kokai) No. 3-292364 as fatty acids, silane coupling agents, esters of fatty acid, phosphoric esters, styrene/maleic anhydride copolymers and their derivatives and titanate coupling agents, or a mixture of these substances.

[0037] Such a surface treating agent is allowed to adhere to the composite oxide particles preferably in an amount of 0.1% or more by weight based on the composite oxide. Sufficient effects cannot be obtained when the amount is less than 0.1% by weight, and no further improved effects can be obtained substantially when the amount exceeds 10% by weight.

[0038] Fatty acids used in the surface treatment are mono- or dicarboxylic acids having a linear or branched alkyl group of 10 to 30 carbon atoms. Examples of the fatty acids include capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid. Esters of fatty acid used in the surface treatment are esters of the fatty acids as mentioned above with mono- or polyvalent alcohols having a linear or branched alkyl group of 1 to 30 carbon atoms. Examples of the fatty acid esters include glyceryl monostearate, stearyl oleate and lauryl oleate. Fatty acids are more effective than esters of fatty acid. Linear or branched fatty acids having from 10 to 20 carbon atoms are particularly preferred, and stearic acid is most preferred.

[0039] Phosphoric esters may be either of monoester type, or of diester type or of a mixture of both types. However, phosphoric esters each having a linear or branched alkyl group, which belong to one ester, of 4 to 30 carbon atoms are preferred. Examples of the phosphoric esters include butyl acid phosphate, 2-ethylhexyl acid phosphate, lauryl acid phosphate, tridecyl acid phosphate, stearyl acid phosphate, di-2-ethylhexyl phosphate and oleyl acid phosphate. Phosphoric acid esters each having a linear or branched alkyl group, which belongs to one ester, of 8 to 20 carbon atoms

(2) a method comprising directly spraying or mixing the composite oxide with the surface treating agent dissolved in an organic solvent, and removing the organic solvent; (3) a method comprising dispersing the composite oxide in a solvent for the polyurethane in which the surface treating agent is dissolved; (4) a method comprising adding the surface treating agent to a polyurethane solution containing the composite oxide, and mixing the surface treating agent with the solution; (5) a method comprising dissolving or dispersing the surface treating agent in finish oil, and allowing the surface treating agent to adhere to the fiber together with the finish oil during spinning and winding an elastic polyurethane fiber; (6) a method comprising treating a plaited knitting composed of an elastic polyurethane fiber containing the composite oxide and a polyamide fiber with a solution in which the surface treating agent is dissolved or dispersed; and (7) other various known methods. The methods by coating (1) to (4) exemplified above and capable of efficiently allowing the surface treating agent to directly adhere to all the composite oxide particles are preferred. The methods (2) to (3) are more preferred.

[0047] Specific examples of allowing the surface treating agent to adhere to the composite oxide particles by coating include the following methods: a method comprising placing the composite oxide in the present invention and 2% by weight based on the composite oxide of stearic acid in a Henschel mixer, heating, and stirring them; a method comprising placing the composite oxide and 4% by weight based on the composite oxide of lauric acid dissolved in methanol in a conical drier, mixing them, and removing methanol; and a method comprising dispersing by a homomixer the composite oxide and 1% by weight based on the composite oxide of an esterified product of a styrene/maleic anhydride copolymer represented by the formula (4)-2 is directly dissolved in dimethylacetamide, a solvent for the polyurethane.

[0048] The procedure of allowing these surface treating agents to adhere to the composite oxide surface at the stage of a spinning dope prior to spinning the elastic polyurethane fiber has the effect of inhibiting secondary agglomeration of the composite oxide particles in the spinning dope in addition to the effect of further improving the durability of the fiber to chlorine subsequent to tannin treatment. Accordingly, the procedure also has the effects of decreasing filter clogging of the spinning dope and diminishing yarn breakage during spinning.

[0049] The polyurethane used in the present invention is produced from, for example, a polymer glycol having hydroxyl groups at both molecular ends and a number average molecular weight of 600 to 5,000, an aromatic diisocyanate and a chain extender having polyfunctional active hydrogen atoms. Examples of the polymer glycol include various diols each composed of a substantially linear homo- or copolymer such as polyester diols, polyether diols, polyester amide diols, polyacryl diols, polythioester diols, polythioether diols and polycarbonate diols, or a mixture of these substances or a copolymer thereof and the like. Examples of the aromatic diisocyanate include 4,4'-diphenylmethane diisocyanate and 2,4-tolylene diisocyanate and the like. Examples of the chain extender having polyfunctional active hydrogen atoms include 1,4-butanediol, ethylene glycol, ethylenediamine, 1,2-propylenediamine, 1,3-diaminocyclohexane, m-xylenediamine, hydrazine, piperazine, dihydrazide and water, or material containing a mixture of these substances and the like as its major component. Known techniques for polyurethane-forming reactions can be applied to the preparation of the polyurethane. For example, a polyalkylene glycol and an aromatic diisocyanate are reacted under the condition that the aromatic diisocyanate is present in an excessive amount, and the reaction products are dissolved in a polar solvent such as dimethylacetamide to give a solution of a polyurethane prepolymer. The prepolymer is subsequently reacted with a chain extender to give the polyurethane.

[0050] The composite oxide in the present invention is usually added to the solution of the polyurethane. However, the composite oxide may also be added to the starting materials of the polyurethane in advance, or it may also be added during the reaction of polyurethane prepolymer or the reaction of chain extension.

[0051] Such compounds other than the composite oxides in the present invention usually used for the elastic polyurethane fiber as ultraviolet ray absorbers, antioxidants, stabilizers, gas-resistant stabilizers, coloring agents, delustering or matting agents and fillers may be added to the solution of polyurethane.

[0052] The solution of polyurethane thus obtained can be formed into a fibrous shape by a known procedure such as dry spinning or wet spinning to give an elastic polyurethane fiber.

[0053] The following substances may be applied to the elastic polyurethane fiber: polydimethylsiloxanes, polyester-modified silicones, polyether-modified silicones, amino-modified silicones, a mineral oil, fine mineral particles such as silica, colloidal alumina and talc and the like, a powder of metal salts of higher fatty acids such as Mg stearate and calcium stearate and the like, and a finish oil, which is solid wax, etc. at room temperature, such as higher aliphatic carboxylic acids, higher aliphatic alcohols, paraffin and polyethylene and the like. These substances may be used singly or in an optional combination thereof.

[0054] The elastic polyurethane fiber of the present invention may be used as a bare spandex yarn without further processing, or it may be used as a covered elastic fiber by covering it with another known fiber such as a polyamide fiber, a polyester fiber, wool, an acrylic fiber, cotton and a regenerated fiber.

[0055] The elastic polyurethane fiber of the present invention can be appropriately used in particular for racing swimwear used in swimming pools. However, the application is not restricted thereto. It can also be used for common swimwear, tights, pantihose, foundation garments, socks, rib tops, corsets, bandages, various sportswear, and the like.

[0056] Various pretreatments and measurement methods for evaluating the properties of the elastic polyurethane

## [6] Evaluation of Spinning Dope with regard to Filter Clogging

[0064] A polyurethane spinning dope is passed through a filter (10  $\mu\text{m}$ , trade name of Naslon Filter, manufactured by Nippon Seisen Co., Ltd.) having a diameter of 10 mm at a constant flow rate of 3 l/hr, and from the dope supply pressures after 0.1 hr and 2 hr, and the filter clogging pressure rise rate  $\Delta P$  is calculated by the formula (7):

$$\Delta P = (P_2 - P_{0.1}) / P_{0.1} \times 100 \quad (7)$$

wherein  $P_{0.1}$  is a dope supply pressure ( $\text{kg}/\text{cm}^2$ ) after supplying the dope for 0.1 hr, and  $P_2$  is a dope supply pressure ( $\text{kg}/\text{cm}^2$ ) after supplying the dope for 2 hr, is determined.

[0065] Larger  $\Delta P$  signifies that the filter clogging is more significant.

## [7] Evaluation of Spinning Stability

[0066] A polyurethane spinning dope is passed through a filter (40  $\mu\text{m}$ , trade name of Naslon Filter, manufactured by Nippon Seisen Co., Ltd.), and the dope is dry spun by extruding the dope through 5 orifices each having a diameter of 0.2 mm to form an elastic polyurethane fiber having 40 denier/5 filaments. The fiber is once wound at a winding rate of 300 m/min for 3 minutes; the winding rate is gradually increased, and the spinning stability is evaluated by a limit denier per single filament calculated from the formula (8):

$$\text{Limit single filament denier (d)} = 40/5 \times 300/X \quad (8)$$

wherein  $X$  is a winding rate (m/min) at the time when yarn breakage takes place within the spinning tube.

[0067] A smaller denier per filament (limit denier per single filament) signifies that the polyurethane is more excellent in spinning stability.

## [8] Evaluation of Chlorine Resistance of 2-Way Tricot Fabric

[0068] A gray fabric is knitted under the following conditions using a bright fiber (manufactured by Mitsubishi Rayon Co., Ltd.) which is prepared from a cation-dyeable ester and has a fineness of 50 denier/17-filaments in the front and an elastic polyurethane fiber in the back: 28 gauges; a front runner of 172 cm; and a back runner of 75 cm. The gray fabric is then set at 190°C for 1 minute, treated with a pH adjusted solution (pH 5) containing 1.7 g/l of acetic acid and 1.0 g/l of sodium sulfate at 95°C for 60 minutes, and subsequently set at 180°C for 1 minute to obtain a finished fabric.

[0069] The knitted fabric is repeatedly immersed in a swimming pool for 12 hours and air dried for 12 hours while being stretched in the weft direction by 80%. The available chlorine concentration is always adjusted to 2.5 ppm during the immersion for 12 hours. In addition, the knitted fabric is washed with service water having an available chlorine concentration of 0.3 ppm, and air-dried for 12 hours as mentioned above. When the knitted fabric is taken out from immersion for 12 hours, it is observed to confirm whether or not it has defects. The number of days until defects are generated in the fabric is defined to be chlorine-durable days of the knitted fabric. A knitted fabric having more chlorine-durable days has a higher chlorine resistance.

## [9] Determination of Anti-Chlorine Agent in 2-Way Tricot Fabric

[0070] A 2-way tricot fabric in an amount of 1 g is incinerated on a platinum plate by heating it with a muffle electric furnace at 400°C for 5 hours. The residue thus formed is dissolved in 30 ml of 50% hydrochloric acid, and filtered, thereby removing insoluble material. The concentration of Zn or Mg is determined by an inductively coupled emission spectrochemical apparatus (ICP, trade name of IRIS/AP type, manufactured by Nippon Jarrel Ash K.K.), and the amount  $F$  of an anti-chlorine agent (g/g of the 2-way tricot fabric) is determined. On the other hand, 5 g of a 2-way tricot fabric is immersed in 300 ml of dimethylacetamide, thereby dissolving the elastic polyurethane fiber in the knitted fabric. The knitted fabric after dissolution is dried at 70°C for 15 hours. From the weight ratio of the knitted fabric subsequent to dissolution to that prior to dissolution, the blending ratio  $W$  (%) of the elastic polyurethane fiber in the 2-way tricot fabric is determined. The content  $E$  (%) of the anti-chlorine agent based on the solid component of the polyurethane is determined from the formula (9):

$$E (\%) = F/(W/100) \quad (9)$$

[0071] The present invention will be concretely explained by making reference to examples. However, the present invention is not restricted thereto.

## Comparative Example 3

5 [0083] An elastic polyurethane fiber was produced in the same manner as in Example 1 except that  $\text{Zn}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 3\text{H}_2\text{O}$  (hydrotalcite) the particles the surface of which had been coated with 1% by weight of stearic acid by the same procedure as in Example 2 was used in place of  $3\text{ZnO} \cdot \text{ZnAl}_2\text{O}_4$  in Example 1.

## Comparative Examples 4 to 6

10 [0084] An elastic polyurethane fiber was produced in the same manner as in Example 1 except that zinc oxide (commercially available, having a high purity of at 99.7% or more and an average particle size of  $1\text{ }\mu\text{m}$  or less) or a solid solution of magnesium oxide and zinc oxide (magnesium oxide/zinc oxide ratio of 65/35) was used in place of  $3\text{ZnO} \cdot \text{ZnAl}_2\text{O}_4$  in Example 1. An elastic polyurethane fiber was produced in the same manner as in Example 1 except that  $3\text{ZnO} \cdot \text{ZnAl}_2\text{O}_4$  was not added.

15 [0085] Tables 1, 2 show the evaluation results of the chlorine resistance, filter clogging of the polyurethane spinning dope and the spinning stability of each of the elastic polyurethane fibers obtained in Examples 1 to 8 and Comparative Examples 1 to 6.

## Example 9

20 [0086] A 2-way tricot fabric was prepared from the elastic polyurethane fiber obtained in Example 1, and its chlorine resistance in a swimming pool was tested.

## Comparative Example 7

25 [0087] A 2-way tricot fabric was prepared from the elastic polyurethane fiber obtained in Comparative Example 4, and its chlorine resistance in a swimming pool was tested.

[0088] Tables 3, 4 show amounts of the anti-chlorine agent retaining in the 2-way tricot fabrics in Example 9 and Comparative Example 7 prior to and subsequent to dyeing, and the results of evaluating the chlorine resistance of the fabrics.

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Table 2 (continued)

|             | Filter clogging caused by spinning dope $\Delta P$ (kg/cm <sup>2</sup> ) | Spinning stability Limit denier per single filament (d)                  | Chlorine resistance tested by immersion in 3 ppm chlorine water after dyeing and treating with tannin solution $\tau_{1/2}$ (Hr) |
|-------------|--|--|--|
| Ex. 2       | 0.4  | 1.2  | 136  |
| Ex. 3       | 0.5  | 1.3  | 85   |
| Ex. 4       | 0.7  | 1.6  | 124  |
| Ex. 5       | 1.3  | 1.7  | 102  |
| Ex. 6       | 0.9  | 1.8  | 103  |
| Ex. 7       | 1.1  | 1.8  | 87   |
| Ex. 8       | 1.8  | 1.9  | 91   |
| Comp. Ex. 1 | 10.2   | Frequent yarn breakage took place. Continuity of spinning was impossible |  |
| Comp. Ex. 2 | 0.9  | 1.3  | 51   |
| Comp. Ex. 3 | 2.0  | 2.2  | 67   |
| Comp. Ex. 4 | 2.5  | 2.4  | 59   |
| Comp. Ex. 5 | 6.4  | 2.6  | 52   |
| Comp. Ex. 6 | 0.2  | 1.2  | 28   |

Table 3

|             | Anti-chlorine agent                   |                   |   | Molar ratio of bivalent metal $M^{2+}$ to Al | Addn. amt. based on polyurethane (wt.%) |
|-------------|---------------------------------------|-------------------|---|--|---|
|             | Hydrotalcite compound (Before firing) | Firing temp. (°C) | Composite oxide obtained by firing hydrotalcite cpd. (after firing) |  |   |
| Ex. 9       | $Zn_4Al_2(OH)_{12}(CO_3) \cdot 3H_2O$ | 900               | $3ZnO \cdot ZnAl_2O_4$  | 2  | 4.0                                     |
| Comp. Ex. 7 | ZnO                                   |                   |   | -  | 4.0                                     |

Table 4

|             | Amount of anti-chlorine agent in 2-way tricot fabric (wt.% based on polyurethane solid component) |                         |                    | Chlorine resistance of 2-way tricot fabric                             |
|-------------|---|-------------------------|--------------------|--|
|             | Gray fabric   | After treatment at pH 5 | Retention rate (%) | Number of days required until formation of defect was observed. (days) |
| Ex. 9       | 4.0   | 3.8                     | 93                 | 41   |
| Comp. Ex. 7 | 4.0   | 1.3                     | 33                 | 26   |

Fig.1

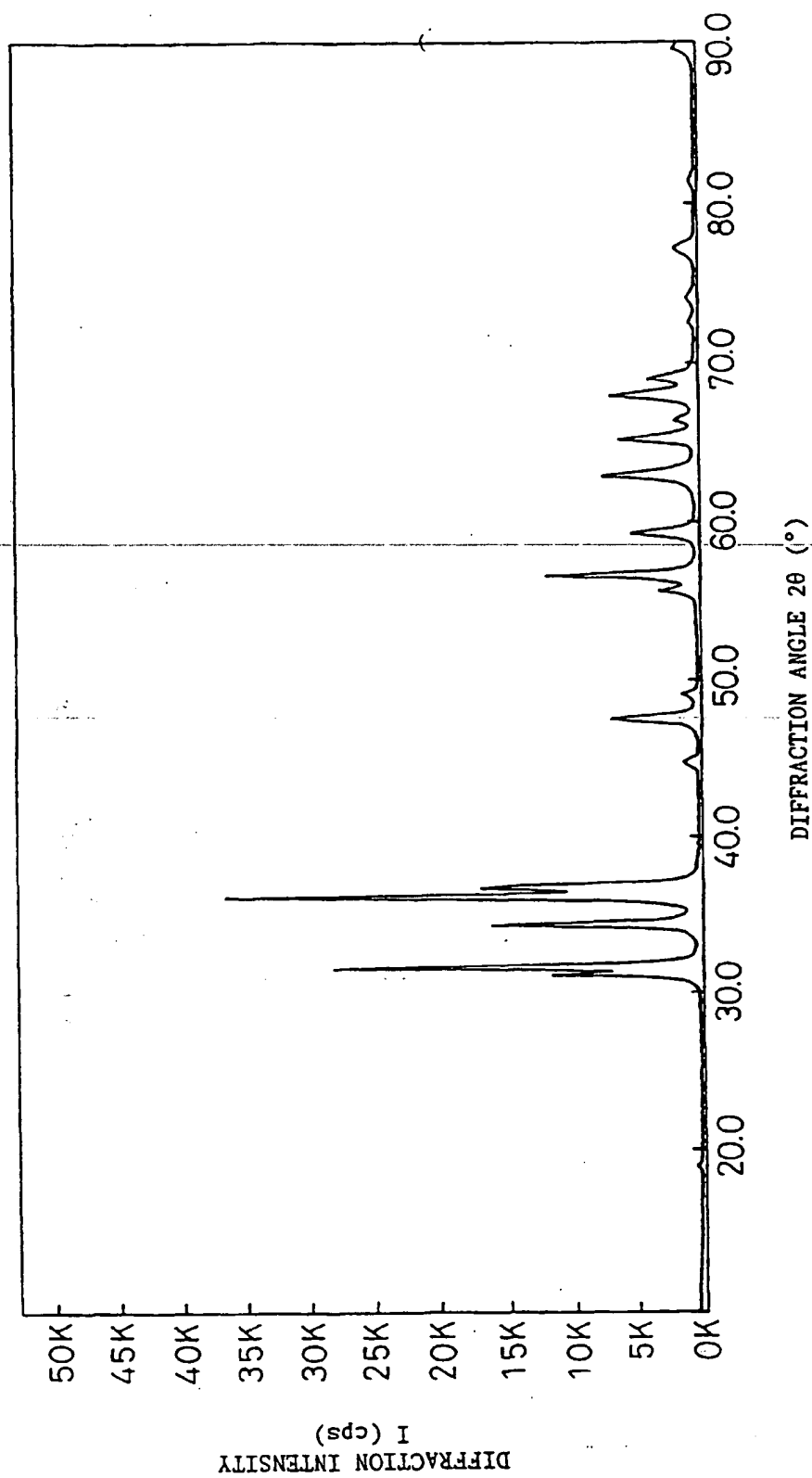




Fig. 3



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/00566

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>6</sup> D01F6/94, D01F1/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>6</sup> D01F6/94, D01F1/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1997 Toroku Jitsuyo Shinan Koho 1994-1997  
 Kokai Jitsuyo Shinan Koho 1971-1996 Jitsuyo Shinan Toroku Koho 1996-1998

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                   | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | JP, 6-41802, A (Suwani K.K.),<br>February 15, 1994 (15. 02. 94) (Family: none)                       | 1-9                   |
| A         | JP, 5-271432, A (Asahi Chemical Industry Co., Ltd.),<br>October 19, 1993 (19. 10. 93) (Family: none) | 1-9                   |
| A         | JP, 6-81215, A (Toyobo Co., Ltd.),<br>March 22, 1994 (22. 03. 94) (Family: none)                     | 1-9                   |

☐ Further documents are listed in the continuation of Box C.
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